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Re: Phase II, First Quarterly Report #ZDJ-2-30630-14

Dear Harin,

This letter comprises the quarterly technical status report for Thin Film Partnership subcontract # ZDJ-2-30630-14. The reported work was performed during the first quarter of year 2 for this contract, from 5/15/03 to 8/15/03. This report describes activities performed by GSE, as well as those performed by lower-tier subcontractor ITN Energy Systems, Inc.

INTRODUCTION

Two-stage and three-stage CIGS coevaporation - followed by chemical bath CdS and RF-sputtered resistive and conductive ZnO - have come to be viewed as laboratory standards for the deposition of CIGS photovoltaic devices. However, a number of conditions are encountered during continuous manufacturing that prevent an exact replication of the laboratory processes. Such differences include both those imposed by continuous processing of moving substrates, and those implemented to decrease costs and increase throughput. It is therefore beneficial to understand the tolerance of the established laboratory processes to variations in deposition procedures.

Research under this program consists of four basic parts to examine the tolerance of the established laboratory process to variations in deposition procedures:

1. Setting up the National Renewable Energy Laboratory (NREL)-developed three-stage CIGS laboratory process in a bell jar.
2. Characterizing the GSE roll-to-roll production chambers and device finishing steps in terms of the variables important to the laboratory processes.
3. Using the bell jar system to step incrementally from the NREL process to the conditions experienced by a sample during manufacturing, and characterizing the resulting films and devices.
4. Applying the process sensitivity information gained from the bell jar system to the production systems.

Some portions of these tasks will be performed in parallel.

PRODUCTION SYSTEM CHARACTERIZATION

Metals Flux Profiles with Se

Experiments were performed to determine the degree and manner in which interaction between the selenium and copper vapor plumes affects the peak intensity and shape of the copper flux distribution at the web under conditions used for CIGS production at GSE. This information is needed to determine how metal flux rates should be varied in an NREL-type bell jar CIGS process with a stationary substrate to simulate the varying flux to the web in the GSE roll-to-roll process.

To best utilize available chamber time, measurements of the copper plume distribution as a function of selenium backpressure were carried out in the intelligent processing (IP) chamber at ITN, using an earlier version of the GSE production sources. The basic approach was to establish a fixed copper effusion rate and selenium back pressure, move a fresh section of web quickly into the deposition zone, stop the web to allow copper (and selenium) to accumulate, move the web quickly out of the deposition zone, and measure the thickness of copper deposited onto the web as a function of position using XRF. To produce results that could be related to processing parameters used at GSE, efforts were made to ensure that both containment of selenium and measurement of the selenium in the IP chamber were as similar as possible to the containment and measurement at GSE.

Prior to the present experiments, the effective degree of selenium containment within the deposition zone of the IP chamber was much less than for the deposition zones at GSE. The main difference was the containment zone floor, which in the IP chamber did not extend over the metal source power feed-throughs as it does in the GSE chambers. The feed-throughs and the chilled based plate near the feed-throughs in the IP chamber therefore had a direct view of the deposition zone, which was otherwise surrounded by hot surfaces on which selenium would not condense. The chilled feed-throughs and baseplate thus provided significant "pumping" (through condensation) of selenium from the deposition zone, which undoubtedly resulted in higher selenium pressure gradients than in the GSE chambers. This was remedied by replacing the containment-zone floor with a larger graphite plate (similar to what is used at GSE) that covered the baseplate throughout the entire selenium containment region. Holes in the graphite plate allowed the power feed-through posts to poke through (with glass insulators to prevent shorting). Note that selenium containment on the top side of the deposition zone was provided by the web itself, which was 12-inch wide steel foil coated with molybdenum by GSE.

During the tests, the substrate heaters were heated to a temperature of 600°C. The indium and gallium sources were heated to temperatures of 770 and 860°C, respectively, which is not hot enough to cause significant effusion of indium or gallium. The copper source was operated under temperature control with a setpoint temperature of 1400°C, which causes effusion at a rate suitable for deposition of a 2 μm-thick CIGS film at a web speed of about 0.75 inches per minute. Note that this effusion rate is much lower than the copper effusion rate used at GSE. Several attempts were made to operate the selenium under PID control, but even with several refinements of the PID parameters, these attempts resulted in undesired oscillations of the Se signal. The final run, from which the data in this report were derived, was performed with the selenium source operated under a different control mechanism. While there were still some minor oscillations, sufficiently long periods with relatively stable Se signal allowed the desired data to be generated.

Imprints of the copper flux distribution were made on the web three times during the run. Each time, this was done as follows:

1. The web was moved forward at 20 inches per minute for at least 28 inches to bring fresh web into the deposition zone.
2. The web was stopped and held in place for a period of 20 minutes.
3. The web was moved forward at 20 inches per minute for at least 28 inches to entirely remove the newly coated section of web from the deposition zone.

This procedure produced sections of the web for which the copper thickness distribution consisted of an imprint of the copper flux distribution superimposed on a uniform background corresponding to the thickness of copper that would be deposited on a web moving continuously through the deposition zone at 20 inches per minute. This assumes that the sticking coefficient for copper vapor incident on the web was uniform and constant and that the copper flux distribution remained constant throughout the 23-minute procedure. The first imprint was made once the Se signal appeared to have stabilized at an intermediate value (termed "level 2 Se flux"). The selenium signal was then increased ("level 3" Se). The second imprint was made over after this adjustment yielded a relatively stable Se signal. The selenium signal was then adjusted once more to allow for the final desired lowest Se signal ("level 1") to stabilize prior to obtaining the last measurement – i.e., making the last imprint.

Following the run, the thicknesses of copper and selenium were measured by XRF for each imprinted region of web along the strip that passed directly over the copper nozzle. These measurements were carried out at intervals of 0.63 inches across the entirety of each of the three imprinted regions.

Thicknesses of copper in the films deposited on the web as measured by XRF are plotted as a function of down-web position for each of the three imprint regions in Figure 1. Positions zero and 27.75 correspond the boundaries of the selenium containment zone. The location of the copper source is also shown. Note, however, that the copper source may not have been precisely level, i.e., its nozzle may not have been completely vertical. This could account for a small offset between the nozzle location and the peak of the thickness distributions. The increase in thickness at the 30-inch position for the level 2 data is because this portion of web was parked in the deposition zone prior to making the imprint. Note that most of the data for positions outside of the deposition zone are at or slightly below zero. This should not strictly be the case, as all parts of the web must have accumulated some copper while traveling through the deposition zone at 20 inches per minute. By integrating the curves in the figure, one can calculate that this minimum amount of accumulation should be between 60 to 80 Å. The discrepancy must be attributed to zero-offset error in the XRF analysis.

The XRF measurements also gave values for the effective thickness of selenium in the films. The selenium and copper thicknesses were combined to determine the ratio of the atomic concentration of selenium to that of copper, as plotted in Figure 2. It is interesting to note that most of the deposited Se exists in either a 1:2 or 1:1 ratio with the Cu. These ratios are the same as those of the compounds Cu_2Se and CuSe, respectively. The very high Se/Cu values at the edges of the distributions may be due to the increased importance of XRF measurement errors to Se/Cu ratio as the Cu thickness approaches 0. No independent phase analysis was performed to identify phases present, as this was not the goal of the investigation.

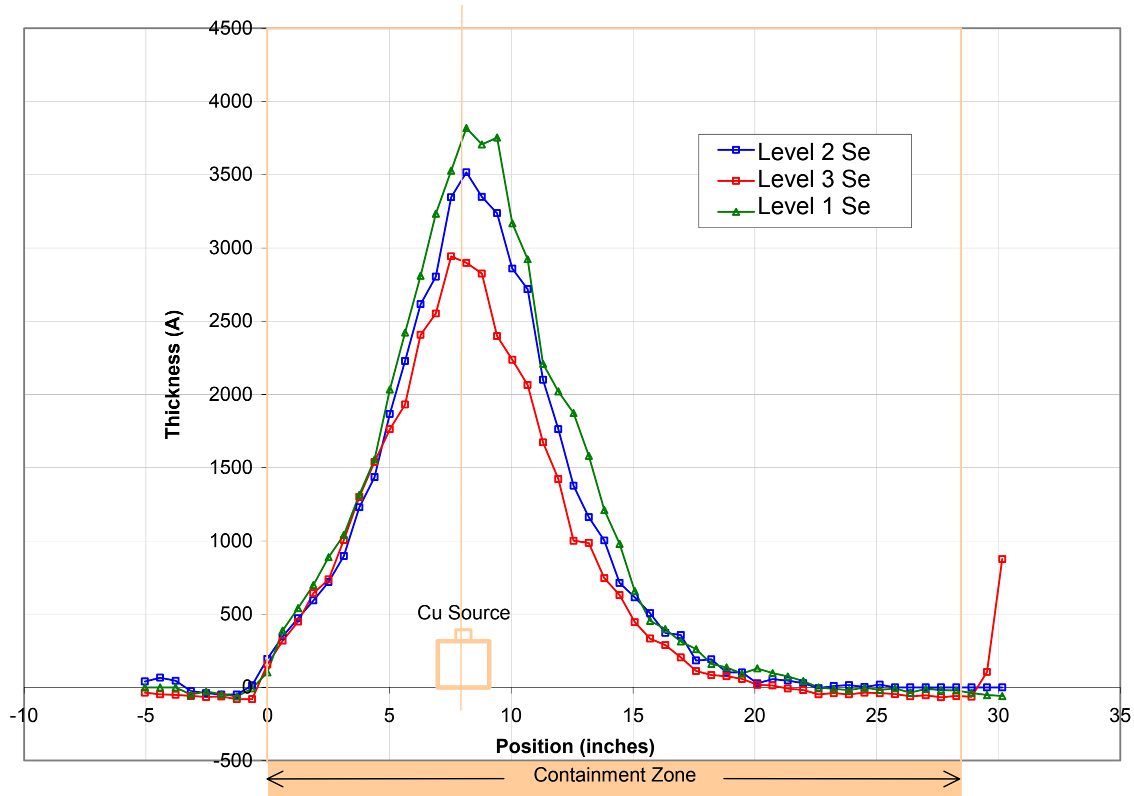

Figure 1: Copper thickness measured by XRF as a function of position for the three ranges during which an imprint was made.

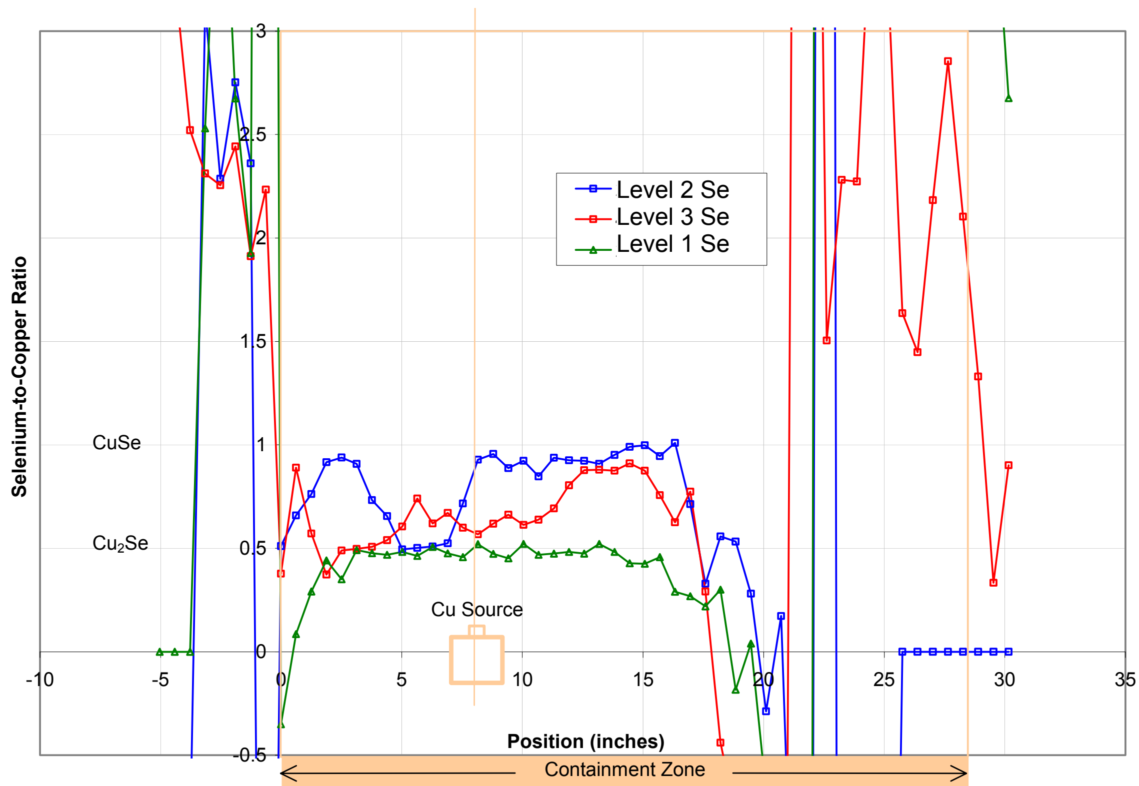

Figure 2: Ratio of selenium-to-copper atomic concentrations as a function of position.

Clearly, the primary observed effect of higher selenium signal on the copper flux was an overall decrease in its intensity. The effect of selenium on the shape of the flux distribution is best seen in Figure 3, in which each flux profile was normalized by its peak value. This figure reveals that there were no significant changes in the shape of the distributions. For the highest-signal range (level 3), there may have been a slight shift towards the up-web side of the deposition zone, although the magnitude of the shift is comparable with the uncertainty in determining the web position (~0.5 inches). As the selenium source is located on the down-web side of the deposition zone, the direction of the observed shift is consistent with displacement of the copper plume due to the directed component of the selenium vapor.

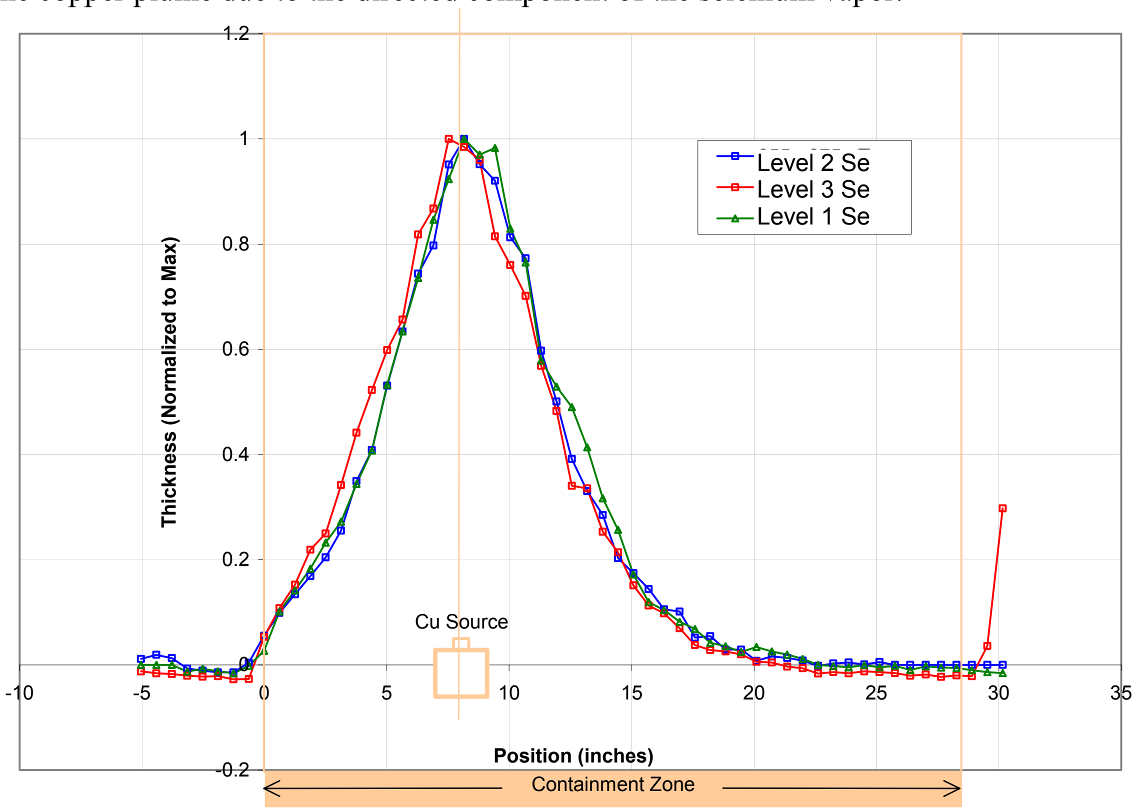

Figure 3: Copper thickness normalized to the peak value for each range.

Measurements at the Institute of Energy Conversion (IEC) using a hoop apparatus have determined that the flux for effusion of copper from a nozzled boat with no selenium present varies as the cube of the cosine of the angle to the nozzle centerline. For the present experiment in which selenium comparable to the amount used at GSE was present, the copper thickness data again exhibit the $\cos^3$ angular dependence. Figure 4 shows the copper thickness data for each signal range together with fits to the data based on a $\cos^3$ angular distribution taking into account the geometric factors that convert the distribution from a function of θ to a function of position along the web. The fitting was performed using data between the 1-inch and 25-inch positions and with the overall magnitude and the center position of the distribution being the only fitting parameters. Fitting was also performed with the exponent of the cosine added to the list of fitting parameters – i.e. the data were fit using a $\cos^n$ angular distribution. The resulting best-fit values are shown in Table 1. The best-fit values for the exponent are very close to 3, and the curves produced from this fit are hardly distinguishable from the $\cos^3$-fit curves shown in Figure 4.

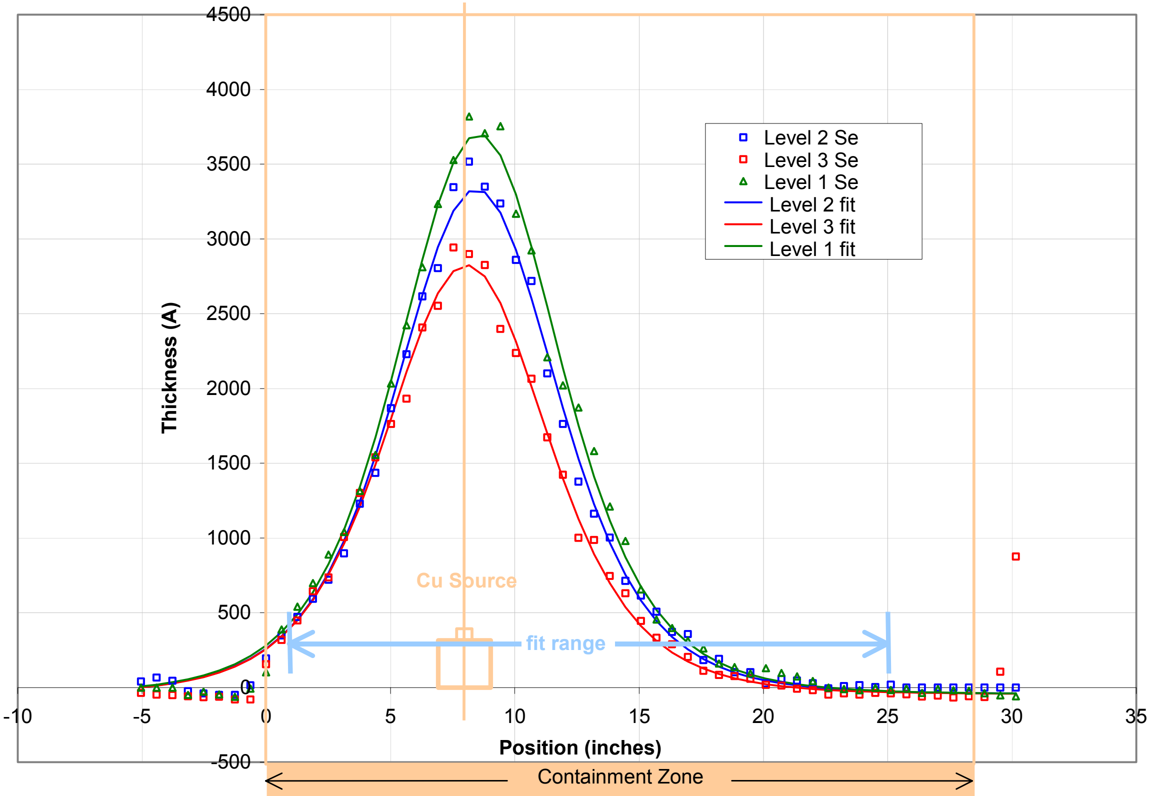

Figure 4: Cosine-cubed flux distributions with magnitudes and peak centers fit to the copper XRF thickness data for each signalrange.

Fit Parameter	*Units*	*level2*	*level3*	*levle1*
Magnitude	Å	3414	2854	3742
Center	Inches	8.45	8.06	8.54
n (exponent)		3.24	2.87	2.97

Table 1: Fit parameter values resulting from fitting copper XRF thickness data to the "cosine^n" flux distribution with the magnitude, peak center, and exponent (i.e. 'n') of the distribution as the only fitting parameters.

Web Temperature

Non-contact methods for monitoring temperatures of the moving web during deposition are under examination. A non-contact measurement is desirable for highest accuracy, given the low thermal mass and low lateral thermal conductivity of the 1 mil steel. Commercial infrared temperature sensors are not applicable, due to both the wavelength dependent CIGS emissivity and the deposition environment. A previously-developed method of deriving temperature from the CIGS visible emission was applied in the bell jar. A first attempt concurrent with CIGS deposition indicated the measurement was affected by the hot Cu plume. Modified sensor positioning to eliminate signal from the plume and further data collection are underway.

LABORATORY EXAMINATIONS

Tolerance of the three-stage process to several variations were examined in the bell jar this quarter. Effect of final Cu/(In+Ga) atomic ratio on device parameters is one such examination. For these experiments, the three-stage process was performed, bringing the sample to a Cu ratio of 1.2 at the end of the second stage. Then, the length of the third stage, delivering only In and Ga, was varied to create films of final Cu ratio ranging from 0.81 to 1.07. Devices were completed with CBD CdS, resistive ZnO, and conductive ITO. Resulting device parameters are shown in Figure 5. Efficiencies are approximately constant for Cu ratios from 0.81 to 0.97, then drop-off sharply as Cu ratio approaches 1. These results confirm those from earlier studies.[1] Cu ratios were measured by x-ray fluorescence prior to device finishing. Efficiencies in Figure 5 are approximately 2% lower than typical device efficiencies from the bell jar due to choice of deposition rates for these experiments.

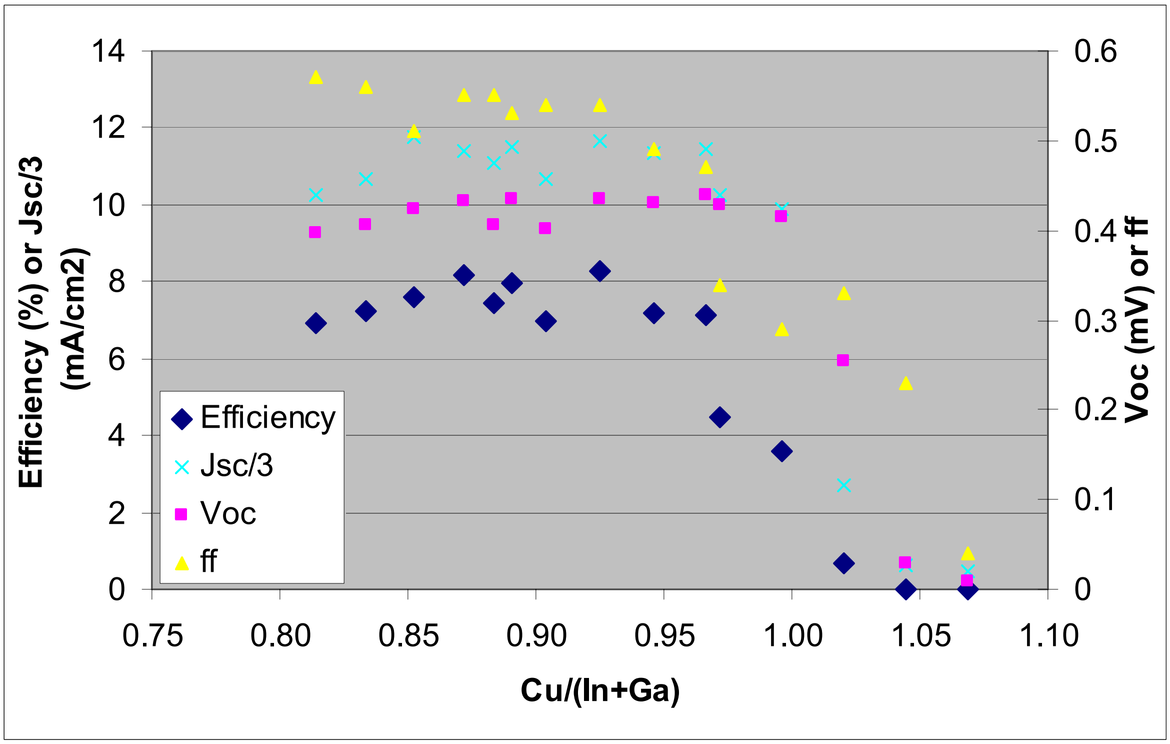

Figure 5: Device parameters as a function of Cu ratio.

Examination of several other process tolerances are also underway. These examinations include temperature variations, and treatment of CIGS surface between CIGS and bath CdS deposition. Variables affecting the CIGS surface involve cool-down and venting temperature, time between venting and CdS, and surface sulfurization via treatments such as thioacetamide.

APPLYING BELL JAR RESULTS TO THE PRODUCTION SYSTEMS

It was described in the Phase I annual report that a novel non-contact method to control the Cu-rich growth excursion had been developed. IR monitoring of the substrate was found to provide unambiguous detection of the Cu-poor to Cu-rich transition, as well as the transition back from Cu-rich to Cu-poor. To date, the sensor has provided accurate and unambiguous non-contact control of the Cu-rich excursion over approximately one hundred high-efficiency CIGS depositions in the bell jar. This quarter, work has begun to determine if this IR monitoring method can be applied to the production systems. Both hardware and analytical challenges exist.

[1] A.M. Gabor, J.R. Tuttle, D.S. Albin, M.A. Contreras, R. Noufi, A.M. Herman, "High-efficiency $CuIn_xGa_{1-x}Se_2$ solar cells made from $(In_x,Ga_{1-x})_2Se_3$ precursor films", *Applied Physics Letters*, **65**(2), (1994), pp. 198-200.

First, the production systems will expose the sensor body to more heat than the bell jar. Second, in the production system, information must be interpreted in a continuous mode, as the sensor sees one portion of the process over and over, rather than seeing all stages consecutively.

PRESENTATION

A summary of GSE's activities related to the Thin Film Partnership was presented at the DOE Photovoltaics Subprogram Peer Review on August 14, 2003.

Best Wishes,

Markus E. Beck

Cc: Carolyn Lopez, NREL Subcontract Associate